

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 649 918 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
20.11.1996 Bulletin 1996/47

(51) Int Cl.⁶: **C25D 3/56**

(21) Application number: **94116560.7**

(22) Date of filing: **20.10.1994**

(54) Alkaline zinc-nickel alloy plating baths

Alkalisches Bad für die galvanische Abscheidung von Zink-Nickel-Legierungen

Bain alcalin de dépôt électrolytique d'alliages zinc-nickel

(84) Designated Contracting States:
DE FR GB SE

(30) Priority: **21.10.1993 US 140588**

(43) Date of publication of application:
26.04.1995 Bulletin 1995/17

(73) Proprietor: **MCGEAN-ROHCO, INC.**
Cleveland Ohio 44113-2251 (US)

(72) Inventors:

- **Block, Dale G.**
Shaker Hts., Ohio 44122 (US)
- **Bishop, Craig V.**
Lakewood, Ohio 44107 (US)

(74) Representative: **VOSSIUS & PARTNER**
Siebertstrasse 4
81675 München (DE)

(56) References cited:
US-A- 4 861 442

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 649 918 B1

Description

This invention relates to aqueous alkaline plating baths and to the electrodeposition of a bright zinc-nickel alloy from such baths. More particularly, the invention relates to alkaline zinc-nickel alloy plating baths containing certain aromatic heterocyclic nitrogen-containing compounds.

Considerable research has been devoted over the years to provide improved corrosion protection to metallic surfaces. One way of providing this corrosion protection is by electrodepositing a zinc coating on the surface. For decades, electroplated zinc has been used by the automotive industry to provide an economical, highly corrosion-resistant coating. However, with continued demands for higher quality and extended warranties, both the automotive manufacturers and their suppliers have had to develop new coatings. The best overall performance is being demonstrated by zinc-cobalt and zinc-nickel alloy platings. These alloys are being used as replacements for conventional zinc electroplates in automotive as well as other applications requiring extended corrosion-resistance. The term "alloy," as used in this specification and claims is defined as a mixture of two or more metallic elements which may be microscopically homogeneous or microscopically heterogeneous.

The improvement of zinc-nickel alloys has been demonstrated by superior salt spray performance when comparing zinc-nickel to zinc electrodeposits. The amount of nickel in the zinc-nickel electrodeposit that is useful for improved corrosion protection has been found to be from about 4% to about 18% nickel with an optimum level of about 10% to 12%.

Typically, acid zinc-nickel alloy plating baths have been based on inorganic zinc and nickel salts such as zinc sulfate, zinc chloride, nickel sulfate or nickel chloride, and the baths contain various additives to improve the brightness and the grain structure of the deposit and provide control of the zinc to nickel ratio.

US-A-2,876,177 describes nickel electroplating baths containing internal salts of quaternary ammonium-N-alkyl sulfonic acids wherein the electroplating baths are Watts-type acid nickel electroplating baths. Acid zinc-nickel alloy plating baths generally contain an acid such as boric acid or sulfuric acid and other additives such as brightening agents, wetting agents, etc. US-A-3,862,019 describes an aqueous acid electroplating bath which contains nickel salts and as brightening agents, the synergistic combination of N-(3-sulfopropyl) pyridinium inner salt and an acetylenic alcohol-ethylene oxide adduct.

US-A-4,421,611 describes an aqueous acidic plating bath for the electrodeposition of nickel or a nickel-iron alloy which comprises nickel ions or a mixture of nickel ions and iron ions, certain acetylenic acid compounds and, optionally, an aromatic heterocyclic nitrogen-containing compound generally referred to as sulfo-betaines.

Aqueous alkaline zinc-nickel alloy plating baths also are known and have been described in the art. For example, US-A-4,861,442 describes aqueous alkaline baths comprising zinc and nickel ions, alkali metal hydroxide, an amino alcohol polymer, a nickel complexing agent, and an amino acid and/or a salt of an amino acid. The pH of the bath is 11 or higher.

US-A-4,877,496 describes aqueous alkaline baths comprising zinc and nickel ions, an alkali metal hydroxide, a metal complexing agent, a primary brightener, and a booster brightener. The primary brightener is a reaction product of an amine such as ethylenediamine with epihalohydrin. The booster brightener is at least one aromatic aldehyde. Tertiary brighteners such as tellurium oxide, tellurous acid or its salts or telluric acid and its salts also can be included in the baths.

US-A-4,889,602 describes aqueous plating baths having a pH of more than 11 and comprising zinc and nickel ions, and at least one compound from the group consisting of (i) aliphatic amines, (ii) polymers of aliphatic amines, or (iii) hydroxyaliphatic carboxylic acids and their salts.

Thus, it is the object of the present invention to overcome the disadvantages of the prior art and to provide an aqueous alkaline plating bath for the electrodeposition of a zinc-nickel alloy coating on a substrate whereby the bath is effective in depositing bright alloys over a wide current density range. This object has been achieved by a plating bath comprising

(A) zinc ions;

(B) nickel ions; and

(C) at least one heterocyclic compound having the general formula I



wherein RN is an aromatic heterocyclic nitrogen-containing group, R¹ is an alkylene or hydroxy alkylene group, Y is -OSO₃, -SO₃, -COOH, -CONH₂ or -OH, X is a halide, a and b = 0 or 1, and the sum of a + b = 1.

Preferably, additional compositions are included in the plating bath to improve the properties of the deposited alloy.

For example, polymers of aliphatic amines may be included to improve the level of the deposits, and metal complexing agents such as hydroxyalkyl-substituted polyamines also may be included.

The improved zinc-nickel alloy electroplating baths of the present invention comprise an aqueous alkaline solution containing zinc ions, nickel ions and at least one aromatic heterocyclic nitrogen-containing compound as described more fully below. The alkaline plating baths are free of cyanide.

The plating baths of the invention contain an inorganic alkaline component in sufficient quantity to provide the bath having the desired pH. Generally, the amount of the alkaline component contained in the plating bath will be an amount sufficient to provide a bath having the desired pH which is generally at least 10, and more often, at least about 11. Amounts of from about 50 to about 220 grams of alkaline component per liter of plating bath may be utilized, and more often, the amount will be from about 90 to about 110 grams per liter. The alkaline component generally is an alkali metal derivative such as sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, etc.

The alkaline plating baths of the present invention generally will contain zinc ion at concentrations ranging from about 1 to about 100 g/l at concentrations of from about 4 to about 30 g/l being preferred. The zinc ion may be present in the bath in the form of a soluble salt such as zinc oxide, zinc sulfate, zinc carbonate, zinc acetate, zinc sulfamate, zinc sulfamate, zinc hydroxide, zinc tartrate, etc.

The plating baths of the present invention also contain from about 0.1 to about 50 g/l of nickel ions, and more often, the bath will contain from about 0.5 to about 20 g/l of nickel ions. Sources of nickel ions which can be used in the plating baths include nickel hydroxide, inorganic salts of nickel, and organic acid salts of nickel. Preferred examples of nickel sources include nickel hydroxide, nickel sulfate, nickel carbonate, ammonium nickel sulfate, nickel sulfamate, nickel acetate, nickel formate, nickel bromide, etc. The nickel and zinc sources which may be used in the plating baths of the invention may comprise one or more of the above-described zinc sources and one or more of the above-described nickel sources.

The plating baths of the invention also contain at least one aromatic heterocyclic nitrogen-containing compound which improves the level and brightness of the zinc nickel alloy deposited from the baths. The aromatic heterocyclic nitrogen-containing compounds are characterized by the formula I



wherein RN is an aromatic heterocyclic nitrogen-containing group, R¹ is an alkylene or hydroxy alkylene group, Y is -OSO₃, -SO₃, -COOH, -CONH₂ or -OH, X is a halide, a and b = 0 or 1, and the sum of a + b = 1.

When a = 1 and b = 0, the heterocyclic compounds are internal salts and may be represented by the formula IA



When a = 0 and b = 1, the heterocyclic compound may be represented by the formula IB



Compounds of the type represented by Formula IA wherein Y is -SO₃ or -OSO₃ are referred to as sulfo-betaines.

Generally, the RN group will be an aromatic nitrogen-containing group such as pyridine, substituted pyridines, quinoline, substituted quinolines, isoquinoline, substituted isoquinolines, and acridines. The aromatic heterocyclic nitrogen-containing group RN may contain two or more nitrogen atoms in the ring. For example, the RN group may be a pyrazine, pyrimidine, or a benzimidazole group. In those instances wherein the RN group contains more than one nitrogen atom, the heterocyclic compound of Formula I, IA and IB may contain two or more of the -R¹-Y⁻ groups. Various substituents can be incorporated into the aromatic nitrogen-containing groups specified above, and the substituent may be attached to the various positions of the aromatic group. Examples of substituents include hydroxy, alkoxy, halide, lower alkyl, lower alkenyl, amino alkyl, mercapto, cyano, hydroxyalkyl, acetyl, benzoyl, etc.

The R¹ group in Formula I, IA and IB, is an alkylene or hydroxy alkylene group generally containing from 1 to about 10 or more carbon atoms, generally in a straight chain. In one embodiment, R¹ is an alkylene or hydroxy alkylene group containing from 2 to 4 carbon atoms in a straight chain. Specific examples of the alkylene and hydroxy alkylene groups (R¹) include ethylene, methylene, propylene, butylene, 2-hydroxy propylene, etc. The Y group present in Formula I, IA and IB may be an -OSO₃, -SO₃, -COOH, -CONH₂ or -OH group or the corresponding alkali metal salts of said groups such as -SO₃Na, -COONa, -COOK, etc. In one embodiment, the heterocyclic compounds (C) wherein Y is OSO₃, SO₃ or COOH may be in the form of the corresponding alkali metal salts produced by reacting the compound with a suitable

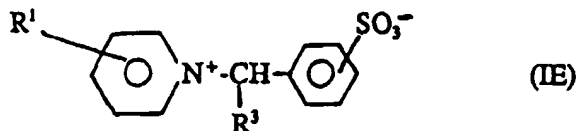
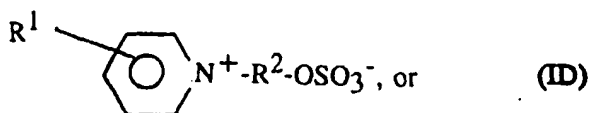
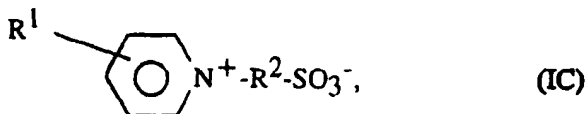
inorganic alkali metal base. This reaction is illustrated with the heterocyclic compounds wherein Y is SO_3 as follows:



In Formulae I and IB, X is a halide. Preferably, X is chlorine.

In one preferred embodiment, the aromatic heterocyclic nitrogen-containing compounds (C) used in the plating baths of the present invention are characterized by Formula IA wherein Y is an $-\text{SO}_3$ or $-\text{OSO}_3$ group. As mentioned, such heterocyclic compounds are referred to as sulfo-betaines.

More particularly the sulfo-betaine compounds can be characterized by the following formulae IC, ID and IE

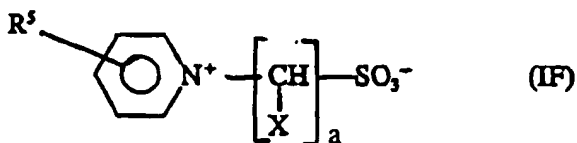


wherein R^1 is hydrogen, benzo(b), or one or more lower alkyl, halide, hydroxy, lower alkenyl or lower alkoxy groups, each R^2 is an alkylene or hydroxy alkylene group containing 3 or 4 carbon atoms in a straight chain, and R^3 is hydrogen or a hydroxyl group.

As can be seen from Formulae IC, ID and IE, the sulfo-betaines contain a pyridinium portion which may be an unsubstituted pyridine ring or a substituted pyridine ring. Thus, R^1 may be one or more lower alkyl groups, halogen groups, lower alkoxy groups, hydroxy groups or lower alkenyl groups.

More specific examples of the pyridine groups which may be included in the above Formulae IC-IE include pyridine, 4-methyl pyridine (picoline), 4-ethyl pyridine, 4-t-butyl pyridine, 4-vinyl pyridine, 3-chloro pyridine, 4-chloro pyridine, 2,3 or 2,4 or 2,6 or 3,5-di-methyl pyridine, 2-methyl-5-ethyl pyridine, 3-methyl pyridine, 3-hydroxy pyridine, 2-methoxy pyridine, 2-vinyl pyridine.

In Formula IC, R^2 can be an alkylene or hydroxy alkylene group containing 3 or 4 carbon atoms in a straight chain which may contain alkyl substituents which may be represented by Formula IF



wherein R^5 is hydrogen or a lower alkyl group, one X is hydrogen, hydroxy or a hydroxy methyl group, the remaining X are hydrogen, and a is 3 or 4.

The preparation of the sulfo-betaines of Formula IC wherein R^2 is an alkylene group is described in, for example, US-A-2,876,177.

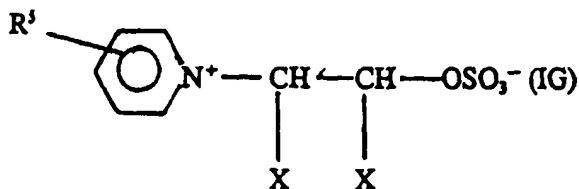
Briefly, the compounds are formed by reaction of pyridine or a substituted pyridine with lower 1,3- or 1,4-alkyl sultones. Examples of such sultones include propane sultone and 1,3- or 1,4-butane sultone. The reaction products formed thereby are internal salts of quaternary ammonium-N-propane-omega-sulfonic acids or the corresponding bu-

tane derivative, depending on the alkyl sulfone used.

The preparation of the sulfo-betaine of Formula IC wherein R^2 is a hydroxy alkylene group is described in, for example, US-A-3,280,130. The method described in this patent involves a first reaction step wherein pyridine is reacted with epichlorohydrin in the presence of hydrochloric acid, and, thereafter, in a second reaction step, the quaternary salt formed thereby is reacted with sodium sulfite.

Preferred examples of the sulfo-betaines wherein R^2 is a hydroxy alkylene group including pyridine compounds of the Formula IF wherein R^5 is hydrogen, one or more lower alkyl groups or a benzo(b) group, a is 3 or 4, one X substituent is a hydroxyl group and the others are hydrogen. In an alternative embodiment, two of the X groups could be hydrogen and the third X group could be a hydroxy alkyl group, preferably, a hydroxy methyl group.

The sulfo-betaines useful in the baths of the invention also include sulfo-betaines of the type represented by Formula ID above wherein R^1 is defined as in Formula I, and R^2 is an alkylene or hydroxy alkylene group containing 2 or 3 carbon atoms in a straight chain and optionally pendant hydroxyl groups, hydroxyl alkyl groups or alkyl groups containing 1 or 2 carbon atoms. Preferred examples of the betaines represented by Formula ID are those wherein R^1 includes compounds of the formula



wherein R^5 is hydrogen, a lower alkyl group or a benzo(b) group, and both X groups are hydrogen or one X is hydrogen and the other is a hydroxyl group.

The preparation of the sulfo-betaines of the type represented by Formulae ID and IG which are known as pyridinium-alkane sulfate betaines is known in the art. For example, the sulfate betaines can be prepared by reacting a pyridine compound with an alkanol compound containing a halogen atom to form an intermediate hydroxyalkyl pyridinium-halide which is thereafter reacted with the corresponding halosulfonic acid to form the desired betaine. Specifically, pyridinium-(ethyl sulfate-2) betaine can be prepared by reacting ethylene chlorohydrin with pyridine followed by reaction with chlorosulfonic acid. The details of the procedure are described in US-A-3,314,868.

Other alkanol compounds containing a halogen which can be reacted with pyridine to form the desired betaines include 1-chloro-2-propanol, 3-chloro-1-propanol, etc.

The useful betaines also include those represented by Formula IE given above which may be obtained by reacting, for example, o-chloro benzyl chloride (prepared from o-chloro benzaldehyde) with pyridine or a substituted pyridine followed by replacement of the o-chloro group with a sulfonic acid group. Although a similar reaction can be conducted with the corresponding meta- and para-chloro compounds, the ortho derivative performs best in the plating baths of the invention.

Specific examples of aromatic heterocyclic nitrogen-containing compounds characterized by Formula I and more particularly Formula IA wherein Y is $-SO_3$ or OSO_3 include the following:

pyridinium-N-propane-3-sulfonic acid
 pyridinium-N-butane-4-sulfonic acid
 pyridinium-N-(2-hydroxy)-propane-3-sulfonic acid
 picolinium-N-propane-3-sulfonic acid
 picolinium-N-butane-4-sulfonic acid
 picolinium-N-(2-hydroxy)-propane-3-sulfonic acid
 2,4-dimethyl-pyridinium-N-propane-3-sulfonic acid
 3-bromo-pyridinium-N-propane-3-sulfonic acid
 quinolinium-N-propane-3-sulfonic acid
 quinolinium-N-butane-4-sulfonic acid
 quinolinium-N-(2-hydroxy)-propane-3-sulfonic acid
 quinaldinium-N-propane-3-sulfonic acid
 acridinium-N-propane-3-sulfonic acid
 pyrocinium-N-ethane-2-sulfate
 pyrazinium-N,N'-di(propane)-3-sulfonic acid

Examples of the aromatic heterocyclic nitrogen-containing compounds of Formula I and IB wherein Y is COOH, CONH₂ or OH include:

N-carboxymethyl pyridinium chloride
 N-carboxymethyl quinolinium chloride
 N-(2-hydroxyethyl) pyridinium chloride
 N-(2-carboxamidoethyl) pyridinium chloride

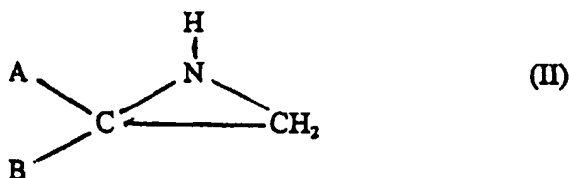
The amount of aromatic heterocyclic nitrogen-containing compound (C) included in the aqueous alkaline plating baths of the present invention is an amount which is sufficient to provide the desired improvement in the level and brightness of the deposited zinc-nickel alloy. Amounts of from about 0.1 to about 20 g/l are usually sufficient to provide the desired improvements. More often, the amount of the heterocyclic nitrogen-containing compound included in the plating baths will be within the range of from about 0.1 to about 10 g/l.

It often is desirable to include in the alkaline plating baths of this invention one or more additional components to provide improved and stable plating baths and to provide for improved zinc-nickel alloys. For example, alkaline plating baths may contain metal-complexing agents, aromatic aldehydes to improve the gloss or brightness of the alloy, polymers of aliphatic amines, surface-active agents, etc.

In one embodiment, the aqueous alkaline plating baths of the present invention will contain (D) at least one polymer of an aliphatic amine. The amount of the polymer of an aliphatic amine contained in the aqueous alkaline plating baths of the present invention may range from about 5 to about 150 g/l and more often will be in the range of from about 25 to about 60 g/l.

Typical aliphatic amines which may be used to form polymers include 1,2-alkyleneimines, monoethanolamine, diethanolamine, triethanolamine, ethylenediamine, diethylenetriamine, imino-bis-propylamine, triethylenetetramine, tetraethylenepentamine, hexamethylenediamine, etc.

Polymers derived from 1,2-alkyleneimines are preferred and the alkyleneimines may be represented by the general formula II



wherein A and B are each independently hydrogen or alkyl groups containing from 1 to about 3 carbon atoms. Where A and B are hydrogen, the compound is ethyleneimine. Compounds wherein either or both A and B are alkyl groups are referred to herein generically as alkyleneimines although such compounds have been referred to also as ethyleneimine derivatives.

Examples of poly(alkyleneimines) which are useful in the present invention include polymers obtained from ethyleneimine, 1,2-propyleneimine, 1,2-butylenimine and 1,1-dimethylethyleneimine. The poly(alkyleneimines) useful in the present invention may have molecular weights of from about 100 to about 100,000 or more although the higher molecular weight polymers are not generally as useful since they have a tendency to be insoluble in the zinc plating baths of the invention. Preferably, the molecular weight will be within the range of from about 100 to about 60,000 and more preferably from about 150 to about 2000. Poly(ethyleneimine)s having molecular weights of from about 150 to about 2000 are preferred examples of poly(alkyleneimines). Useful polyethyleneimines are available commercially from, for example, BASF under the designations Lugalvan® G-15 (molecular weight 150), Lugalvan® G-20 (molecular weight 200) and Lugalvan® G-35 (molecular weight 1400).

The poly(alkyleneimines) may be used per se or may be reacted with a cyclic carbonate consisting of carbon, hydrogen and oxygen atoms. A description of the preparation of examples of such reaction products is found in US-A-2,824,857 and US-A-4,162,947.

The cyclic carbonates further are defined as containing ring oxygen atoms adjacent to the carbonyl grouping which are each bonded to a ring carbon atom, and the ring containing said oxygen and carbon atoms has only 3 carbon atoms and no carbon-to-carbon unsaturation.

Useful metal-complexing agents (E) which can be incorporated into the aqueous alkaline plating baths of the present invention include carboxylic acids such as citric acid, tartaric acid, gluconic acid, alpha-hydroxybutyric acid, sodium or potassium salts of said carboxylic acids; polyamines such as ethylenediamine, triethylenetetramine; amino

alcohols such as N-(2-aminoethyl)ethanolamine, 2-hydroxyethylaminopropylamine, N-(2-hydroxyethyl)ethylenediamine; etc. When included in the baths of the invention, the amount of metal complexing agent may range from 5 to about 100 g/l, and more often the amount will be in the range of from about 10 to about 30 g/l.

A group of metal complexing agents which is particularly useful in the aqueous alkaline plating baths of the present invention is represented by the formula III



wherein R^3 , R^4 , R^5 and R^6 are each independently alkyl or hydroxyalkyl groups provided that at least one of R^3 - R^6 is a hydroxyalkyl group, and R^2 is a hydrocarbylene group containing up to about 10 carbon atoms. The groups R^3 - R^6 may be alkyl groups containing from 1 to 10 carbon atoms, more often alkyl groups containing from 1 to 5 carbon atoms, or these groups may be hydroxyalkyl groups containing from 1 to 10 carbon atoms, preferably from 1 to about 5 carbon atoms. The hydroxyalkyl groups may contain one or more hydroxyl groups, and preferably at least one of the hydroxyl groups present in the hydroxyalkyl groups is a terminal group. In one preferred embodiment, R^3 , R^4 , R^5 and R^6 are hydroxyalkyl groups.

Specific examples of metal complexing agents characterized by Formula III include N-(2-hydroxyethyl)-N,N',N'-triethylethylenediamine; N,N'-di(2-hydroxyethyl)N,N'-diethyl ethylenediamine; N,N-di(2-hydroxyethyl)-N',N'-diethyl ethylenediamine; N,N,N',N'-tetrakis(2-hydroxyethyl)ethylenediamine; N,N,N',N'-tetrakis(2-hydroxyethyl)propylenediamine; N,N,N',N'-tetrakis(2,3-dihydroxypropyl)ethylenediamine; N,N,N',N'-tetrakis(2,3-dihydroxypropyl)propylenediamine; N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine; N,N,N',N'-tetrakis(2-hydroxyethyl)1,4-diaminobutane; etc. An example of a commercially available metal complexing agents useful in this invention includes Quadrol® from BASF. Quadrol is N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine.

Examples of aldehydes which may be included in the plating baths to achieve further improvements in gloss, leveling, etc. include aromatic aldehydes such as anisaldehyde, 4-hydroxy-3-methoxybenzaldehyde (vanillin), 1,3-benzodioxole-5-carboxyaldehyde (piperonal), verateraldehyde, p-tolualdehyde, benzaldehyde, O-chlorobenzaldehyde, 2,3-dimethoxybenzaldehyde, salicylaldehyde, cinnamaldehyde, adducts of cinnamaldehyde with sodium sulfite, etc. The amount of aldehyde which may be included in the plating baths may range from about 0.01 to about 2 g/l.

The aqueous alkaline plating baths of the invention can be prepared by conventional methods, for example, by adding the specific amounts of the above-described components to water. The amount of the alkali metal base compound such as sodium hydroxide which is included in the mixture should be sufficient to provide the bath with the desired pH of at least 10 and preferably above 11.

The aqueous alkaline plating baths of the present invention deposit a bright, level and ductile zinc-nickel alloy on substrates and any conventional temperature such as from about 25°C to about 60°C. Generally, temperatures of about 40°C are utilized. At these temperatures, the plating baths of the invention are stable and effective in depositing bright level deposits over current density ranges of from about 0.54 to about 118.4 mA/cm² (about 0.5 ASF to about 110 ASF.)

The plating baths of the invention may be operated on a continuous or intermittent basis, and from time to time, the components of the bath may have to be replenished. The various components may be added singularly as required or may be added in combination. The amounts of the various compositions to be added to the plating bath may be varied over a wide range depending on the nature and the performance of the zinc-nickel plating baths to which the composition is added. Such amounts can be determined readily by one skilled in the art.

The aqueous alkaline plating baths of the invention can be used over substantially all kinds of substrates on which a zinc-nickel alloy can be deposited. Examples of useful substrates include those of mild steel, spring steel, chrome steel, chrome-molybdenum steel, copper, copper-zinc alloys, etc.

The following examples illustrate the aqueous alkaline plating baths of the invention. The amounts of the components in the following examples are in grams/liter. Unless otherwise indicated in the specification and claims, all parts and percentages are by weight, temperatures are in degrees centigrade, and pressures are at or near atmospheric pressure. In the following examples, the source of zinc ions is zinc oxide in caustic soda, and the source of nickel ions is nickel sulfate.

Example 1

An aqueous plating bath is prepared which contains the following components:

EP 0 649 918 B1

Component	g/l
Zinc ions	8
Nickel ions	2.2
Sodium hydroxide	100
Polyethyleneimine (Lugalvan® G-20)	40
Quadrol®	20
Pyridinium-N-propane-3-sulfonic acid	1.25

The efficacy of this aqueous alkaline plating bath and the method of utilizing such a bath for plating substrates is demonstrated by plating 10.16 x 6.98 cm (4 x 2.75 inch) steel panels at 2 amps for 15 minutes in a Hull Cell with no agitation at about 40°C. The plating bath produces a bright zinc-nickel alloy deposit over the entire current density range of from 0.54 to 118.4 mA/cm² (0.5 ASF to 110 ASF.)

Example 2

Zinc ions	8
Nickel ions	2.2
Sodium hydroxide	100
Lugalvan® G-20	40
Quadrol®	20
Carboxymethylpyridinium chloride	1.7

Steel panels are electroplated in a Hull Cell at 2 amps for 15 minutes at a temperature of about 40°C. A good bright deposit is obtained over the entire current density range.

Example 3

Zinc ions	8
Nickel ions	2.2
Sodium hydroxide	100
Lugalvan® G-20	40
Quadrol®	20
Pyridinium-N-butane-4-sulfonic acid	1.5

Steel panels are plated in a Hull Cell at 2 amps for 15 minutes at a temperature of about 40°C and an excellent bright deposit is produced over the entire current density range.

Example 4

Zinc ions	8
Nickel ions	2.2
Sodium hydroxide	100
Lugalvan® G-20	40
Quadrol®	20
Pyridinium-N-(2-hydroxy)propane-3-sulfonic acid	1.7

A bright zinc-nickel alloy coating is obtained when steel panels are plated in a Hull Cell at 2 amps for 15 minutes at a temperature of about 40°C utilizing this plating bath.

EP 0 649 918 B1

Example 5

Zinc ions	8
Nickel ions	2.2
Sodium hydroxide	100
Polyethyleneimine (Lugalvan® G-35)	40
Quadrol®	20
Carboxymethyl pyridinium chloride	1.5

Example 6

Zinc ions	8
Nickel ions	2.0
Sodium hydroxide	90
Polyethyleneimine (Lugalvan® G-35)	35
Quadrol®	10
2-hydroxyethyl pyridinium chloride	2

Example 7

Zinc ions	15
Nickel ions	3
Sodium hydroxide	100
Polyethyleneimine (Lugalvan® G-15)	45
Quadrol®	10
2-carboxamidoethyl pyridinium chloride	1.5
Sodium tartrate	5

Example 8

Zinc ions	8
Nickel ions	2.2
Sodium hydroxide	100
Lugalvan® G-20	40
N,N,N',N'-Tetrakis-(2-hydroxyethyl)ethylenediamine (THEED)	20
Pyridinium-N-Propane-3-Sulfonic Acid	1.25

Steel panels are electroplated in a Hull Cell at 2 amps for 15 minutes at a temperature of about 40°C. An excellent bright deposit is obtained over the entire current density range.

Example 9

Zinc ions	8
Nickel ions	2.2
Sodium hydroxide	100
Lugalvan® G-20	40
N,N,N',N'-Tetrakis-(2-hydroxyethyl)-ethylenediamine (THEED)	20
Carboxymethyl pyridinium chloride	1.7

Steel panels are electroplated in a Hull Cell at 2 amps for 15 minutes at a temperature of about 40°C. A good bright deposit is obtained over the entire current density range.

Example 10

Zinc ions	8
Nickel ions	2.4
Sodium hydroxide	100
Lugalvan® G-20	40
N,N,N',N'-Tetrakis-(2,3-dihydroxypropyl)-ethylenediamine	20
Pyridinium-N-propane-3-sulfonic acid	1.25

Steel panels are electroplated in a Hull Cell at 2 amps for 15 minutes at a temperature of about 40°C. An excellent bright deposit is produced over the entire current density range.

Example 11

Zinc ions	8
Nickel ions	2.2
Sodium hydroxide	100
Polyethyleneimine (Lugalvan® G-35)	40
N,N,N',N'-Tetrakis-(2,3-dihydroxypropyl)-ethylenediamine	20
Pyridinium-N-(2-hydroxy)-propane-3-sulfonic acid	1.7

A bright zinc nickel alloy coating is obtained on steel panels plated in a Hull Cell at 2 amps for 15 minutes at a temperature of about 40°C utilizing this plating bath.

Claims

1. An aqueous alkaline plating bath for the electrodeposition of a zinc-nickel alloy coating on a substrate which comprises

- (A) zinc ions;
 (B) nickel ions; and
 (C) at least one heterocyclic compound having the general formula



wherein RN is an aromatic heterocyclic nitrogen-containing group, R¹ is an alkylene or hydroxy alkylene group, Y is -OSO₃, -SO₃, -COOH, -CONH₂ or -OH, X is a halide, a and b = 0 or 1, and the sum of a + b = 1.

2. The plating bath of claim 1 wherein Y is -OSO₃ or SO₃, a = 1, and b = 0.
3. The plating bath of claim 1 wherein Y is -COOH, -CONH₂ or -OH, a = 0 and b = 1
4. The plating bath of any of claims 1 to 3 wherein RN⁺ is a pyridinium group
5. The plating bath of any of claims 1 to 4 wherein R¹ is an alkylene or hydroxy alkylene group containing from 1 to about 5 carbon atoms.
6. The plating bath of any of claims 1 to 5 wherein the bath also contains
 (D) at least one polymer of an aliphatic amine.

7. The plating bath of claim 6 wherein the polymer is a poly(alkyleneimine).
8. The plating bath of claim 6 wherein the polymer is a polyethyleneimine.
9. The plating bath of any of claims 1 to 8 wherein the bath also contains (E) at least one metal-complexing agent characterized by the formula III



wherein R³, R⁴, R⁵ and R⁶ are each independently alkyl or hydroxyalkyl groups provided that at least one of R³-R⁶ is a hydroxy alkyl group, and R² is a hydrocarbylene group containing up to 10 carbon atoms, preferably 1 to 5 carbon atoms.

10. The plating bath of claim 9 wherein the hydrocarbylene group R² is an alkylene group containing from 1 to 10 carbon atoms.
11. The plating bath of claim 9 or 10 wherein R³, R⁴, R⁵ and R⁶ in Formula III are hydroxyalkyl groups.
12. The plating bath of any of claims 1 to 11 which comprises

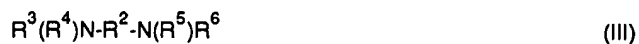
- (A) from 1 to 100 g/l of zinc ions;
- (B) from 0.1 to 50 g/l of nickel ions; and
- (C) from 0.1 to 20 g/l of at least one heterocyclic compound having the general formula I as defined in claim 1.

13. The alkaline plating bath of any of claims 6 to 8 wherein the polymer of an aliphatic amine (D) is present in an amount from 5 to 150 g/l.
 14. The plating bath of any of claims 9 to 11 wherein the metal complexing agent (E) is present in an amount from 5 to 100 g/l.
 15. An aqueous alkaline plating bath for the electrodeposition of a zinc-nickel alloy coating on a substrate which comprises
- (A) from 1 to 100 g/l of zinc ions;
 - (B) from 0.1 to 50 g/l of nickel ions;
 - (C) from 0.1 to 10 g/l of at least one heterocyclic compound having the general formula



wherein RN is an aromatic heterocyclic nitrogen-containing group, R¹ is an alkylene or hydroxy alkylene group and Y is -SO₃, -COOH, -CONH₂ or -OH;

- (D) from 5 to 150 g/l of a poly(alkyleneimine); and
- (E) from 5 to 100 g/l of at least one polyamine metal-complexing agent characterized by the formula



wherein R² is a hydrocarbylene group containing up to 10 carbon atoms, and R³, R⁴, R⁵ and R⁶ are each independently hydroxyalkyl groups.

16. The method of electrodepositing a bright and level zinc-nickel alloy coating on a substrate which comprises electroplating said substrate with the aqueous alkaline plating bath of any of claims 1 to 15.

Patentansprüche

1. Wäßriges alkalisches Plattierungsbad zum galvanischen Abscheiden einer Zink-Nickel-Legierungsschicht auf einem Substrat, umfassend

- (A) Zink-Ionen;
(B) Nickel-Ionen; und
(C) mindestens eine heterocyclische Verbindung der allgemeinen Formel



in der RN ein aromatischer heterocyclischer stickstoffhaltiger Rest ist, R¹ ein Alkyl- oder Hydroxyalkylrest ist, Y für -OSO₃, -SO₃, -COOH, -CONH₂ oder -OH steht, X ein Halogenatom ist, a und b gleich 0 oder 1 sind und die Summe von a + b = 1 ist.

2. Plattierungsbad nach Anspruch 1, wobei Y für -OSO₃ oder -SO₃ steht, a = 1 und b = 0 ist.
3. Plattierungsbad nach Anspruch 1, wobei Y für -COOH, -CONH₂ oder -OH steht, a = 0 und b = 1 ist.
4. Plattierungsbad nach einem der Ansprüche 1 bis 3, wobei RN⁺ eine Pyridiniumgruppe ist.
5. Plattierungsbad nach einem der Ansprüche 1 bis 4, wobei R¹ ein Alkyl- oder Hydroxyalkylrest ist, der 1 bis etwa 5 Kohlenstoffatome enthält.
6. Plattierungsbad nach einem der Ansprüche 1 bis 5, wobei das Bad ferner enthält:
(D) mindestens ein Polymer eines aliphatischen Amins.
7. Plattierungsbad nach Anspruch 6, wobei das Polymer ein Polyalkylenimin ist.
8. Plattierungsbad nach Anspruch 6, wobei das Polymer ein Polyethylenimin ist.
9. Plattierungsbad nach einem der Ansprüche 1 bis 8, wobei das Bad ferner enthält:
(E) mindestens ein Metallkomplexierungsmittel, gekennzeichnet durch die Formel III



wobei R³, R⁴, R⁵ und R⁶ jeweils unabhängig voneinander Alkyl- oder Hydroxyalkylreste sind, mit der Maßgabe, daß mindestens einer der Reste R³ bis R⁶ ein Hydroxyalkylrest ist, und wobei R² ein ungesättigter Kohlenwasserstoffrest mit bis zu 10 Kohlenstoffatomen, vorzugsweise 1 bis 5 Kohlenstoffatomen, ist.

10. Plattierungsbad nach Anspruch 9, wobei der ungesättigte Kohlenwasserstoffrest R² ein Alkylrest mit 1 bis 10 Kohlenstoffatomen ist.
11. Plattierungsbad nach Anspruch 9 oder 10, wobei R³, R⁴, R⁵ und R⁶ in Formel III Hydroxyalkylreste sind.
12. Plattierungsbad nach einem der Ansprüche 1 bis 11, umfassend
- (A) 1 bis 100 g/l Zink-Ionen
(B) 0,1 bis 50 g/l Nickel-Ionen und
(C) 0,1 bis 20 g/l mindestens einer heterocyclischen Verbindung der in Anspruch 1 definierten allgemeinen Formel I.
13. Alkalisches Plattierungsbad nach einem der Ansprüche 6 bis 8, wobei das Polymer eines aliphatischen Amins (D) in einer Menge von 5 bis 150 g/l vorliegt.

14. Plattierungsbad nach einem der Ansprüche 9 bis 11, wobei das Metallkomplexierungsmittel (E) in einer Menge von 5 bis 100 g/l vorliegt.

15. Wäßriges alkalisches Plattierungsbad zum galvanischen Abscheiden einer Zink-Nickel-Legierungsschicht auf einem Substrat, umfassend

(A) 1 bis 100 g/l Zink-Ionen

(B) 0,1 bis 50 g/l Nickel-Ionen

(C) 0,1 bis 10 g/l mindestens einer heterocyclischen Verbindung der allgemeinen Formel



in der RN ein aromatischer heterocyclischer stickstoffhaltiger Rest ist, R¹ ein Alkyl- oder Hydroxyalkylrest ist und Y für -SO₃, -COOH, -CONH₂ oder -OH steht

(D) 5 bis 150 g/l eines Polyalkylenamins und

(E) 5 bis 100 g/l mindestens eines Polyamin-Metallkomplexierungsmittels, gekennzeichnet durch die Formel III



in der R² ein ungesättigter Kohlenwasserstoffrest mit bis zu 10 Kohlenstoffatomen ist und R³, R⁴, R⁵ und R⁶ jeweils unabhängig voneinander Hydroxyalkylreste sind.

16. Verfahren zum galvanischen Abscheiden einer glänzenden und ebenen Zink-Nickel-Legierungsschicht auf ein Substrat, umfassend das Galvanisieren des Substrates mit dem wäßrigen alkalischen Plattierungsbad nach einem der Ansprüche 1 bis 15.

Revendications

1. Bain de dépôt électrolytique alcalin aqueux pour le dépôt électrolytique d'un revêtement d'alliage de zinc-nickel sur un substrat qui comprend :

(A) des ions zinc ;

(B) des ions nickel ; et

(C) au moins un composé hétérocyclique présentant la formule générale



dans laquelle RN est un groupe hétérocyclique aromatique contenant de l'azote, R¹ est un groupe alkylène ou hydroxyalkylène, Y est -OSO₃, -SO₃, -COOH, -CONH₂ ou -OH, X est un halogénure, a et b = 0 ou 1, et la somme a + b = 1.

2. Bain de dépôt électrolytique selon la revendication 1, dans lequel Y est -OSO₃ ou SO₃, a = 1, et b = 0.

3. Bain de dépôt électrolytique selon la revendication 1, dans lequel Y est -COOH, -CONH₂ ou -OH, a = 0 et b = 1.

4. Bain de dépôt électrolytique selon l'une quelconque des revendications 1 à 3, dans lequel RN⁺ est un groupe pyridinium.

5. Bain de dépôt électrolytique selon l'une quelconque des revendications 1 à 4, dans lequel R¹ est un groupe alkylène ou hydroxyalkylène contenant de 1 à environ 5 atomes de carbone.

6. Bain de dépôt électrolytique selon l'une quelconque des revendications 1 à 5, dans lequel le bain contient également

(D) au moins un polymère d'une amine aliphatique.

7. Bain de dépôt électrolytique selon la revendication 6, dans lequel le polymère est une poly(alkylèneimine).

8. Bain de dépôt électrolytique selon la revendication 6, dans lequel le polymère est une poly(éthylène-imine).

9. Bain de dépôt électrolytique selon l'une quelconque des revendications 1 à 8, dans lequel le bain contient également

(E) au moins un agent complexant un métal caractérisé par la formule III



dans laquelle R^3 , R^4 , R^5 et R^6 sont chacun indépendamment des groupes alkyle ou hydroxyalkyle à condition qu'au moins un parmi R^3 - R^6 est un groupe hydroxy alkyle, et R^2 est un groupe hydrocarbyle contenant jusqu'à 10 atomes de carbone, de préférence de 1 à 5 atomes de carbone.

10. Bain de dépôt électrolytique selon la revendication 9, dans lequel le groupe hydrocarbyle R^2 est un groupe alkyle contenant de 1 à 10 atomes de carbone.

11. Bain de dépôt électrolytique selon la revendication 9 ou 10, dans lequel R^3 , R^4 , R^5 et R^6 dans la formule III sont des groupes hydroxyalkyles.

12. Bain de dépôt électrolytique selon l'une quelconque des revendications 1 à 11 qui comprend

(A) de 1 à 100 g/l d'ions zinc ;

(B) de 0,1 à 50 g/l d'ions nickel ; et

(C) de 0,1 à 20 g/l d'au moins un composé hétérocyclique présentant la formule générale I comme définie dans la revendication 1.

13. Bain de dépôt électrolytique alcalin selon l'une quelconque des revendications 6 à 8 dans lequel le polymère d'une amine aliphatique

(D) est présent dans une quantité de 5 à 150g/l.

14. Bain de dépôt électrolytique selon l'une quelconque des revendications 9 à 11, dans lequel l'agent complexant un métal

(E) est présent dans une quantité de 5 à 100g/l.

15. Bain de dépôt électrolytique aqueux alcalin pour le dépôt électrolytique d'un revêtement d'alliage de zinc-nickel sur un substrat qui comprend

(A) de 1 à 100g/l d'ions zinc ;

(B) de 0,1 à 50g/l d'ions nickel ;

(C) de 0,1 à 10 g/l d'au moins un composé hétérocyclique présentant la formule générale



dans laquelle RN est un groupe hétérocyclique aromatique contenant de l'azote, R^1 est un groupe alkyle ou hydroxyalkyle et Y est $-SO_3$, $-COOH$, $-CONH_2$ ou $-OH$;

(D) de 5 à 150g/l d'une poly(alkylèneimine); et

(E) de 5 à 100 g/l d'au moins un agent complexant un métal de polyamine caractérisé par la formule



EP 0 649 918 B1

dans laquelle R^2 est un groupe hydrocarbyle contenant jusqu'à 10 atomes de carbone, et R^3 , R^4 , R^5 et R^6 sont chacun indépendamment des groupes hydroxyalkyles.

- 5 **16.** Procédé de dépôt électrolytique d'un revêtement d'alliage de zinc-nickel brillant et plat sur un substrat qui comprend la métallisation par électrolyse dudit substrat avec le bain de dépôt électrolytique alcalin aqueux de l'une quelconque des revendication 1 à 15.

10

15

20

25

30

35

40

45

50

55